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NOVEL ORGANO-SOLUBLE OPTICALLY TUNABLE CHIRAL HYBRID GOLD NANORODS

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Final Report

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FINAL REPORT

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ABSTRACT (SUMMARY)

The team led by PI Quan Li has conceptualized and rationally synthesized many novel functional hybrid gold nanorods (GNRs) and liquid crystal media. Now this project has accomplished all the proposed objectives and beyond. Organo-soluble chiral azo thiol monolayer-protected gold nanorods, the first of its kind, were synthesized and characterized. More importantly, the chirality of the hybrid GNRs was optically tunable. Moreover, organo-soluble porphyrin mixed monolayer-protected GNRs, porphyrin Zn, Cu and Mg complex monolayer-protected GNRs, and organo-soluble perylene thiol monolayer-protected GNRs were for the first time synthesized and characterized; the controllable self-assembling of GNRs via on and off supramolecular noncovalent interactions was successfully demonstrated; and the photo-modulated self-assembly of hydrophobic thiol monolayer-protected GNRs and their alignment in liquid crystal media was achieved. Furthermore, 3D layer-by-layer graphene-gold nanoparticle hybrid architecture with tunable interlayer distance was for the first time built. Also, near-infrared light-directing transformation of 3D self-organized cubic nanostructures enabled by mesogen-functionalized gold nanorods was for the first time demonstrated. In close collaboration with the groups in Air Force Research Laboratory at Wright-Patterson Air Force Base, this project has opened new avenues with tremendous opportunities and challenges for further exploration. This project has led to 39 publications in which 24 papers are coauthored with the collaborators at AFRL.

Accomplishments/New Findings

- **Organo-soluble chiral azo thiol monolayer-protected gold nanorods**, the first of its kind, were synthesized and characterized. The resulting gold nanorods respectively encapsulated with the two opposite enantiomers over the entire surface via the Au-S linkage, which were found to be very stable in both organic solution and solid state, do have chirality. The chirality of thiol monolayer-protected gold nanorods was optically tunable. The research result is extremely inspiring, which provide a concept demonstration for tuning their properties of practical significance by using functionalized thiol surfactants.

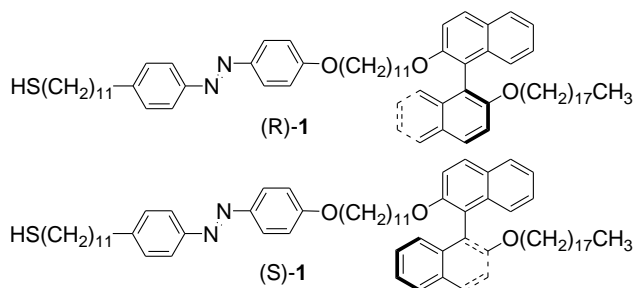


Figure Chemical structure of chiral thiol azo surfactants (R)-1 and (S)-1

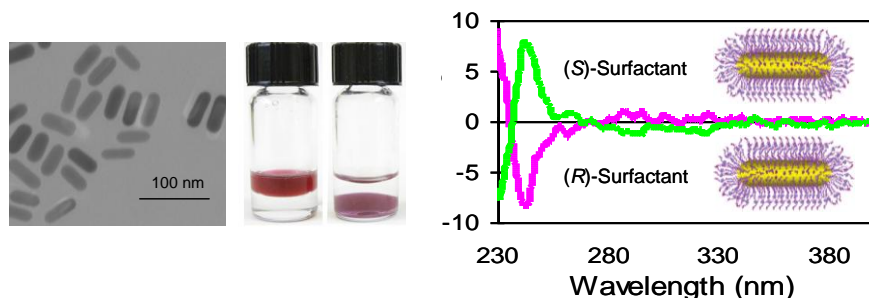


Figure Circular dichroism (CD) spectra of (*R*)-**1** monolayer-protected gold nanorods in CH₂Cl₂ (pink) and (*S*)-**1** monolayer-protected gold nanorods in CH₂Cl₂ (green)

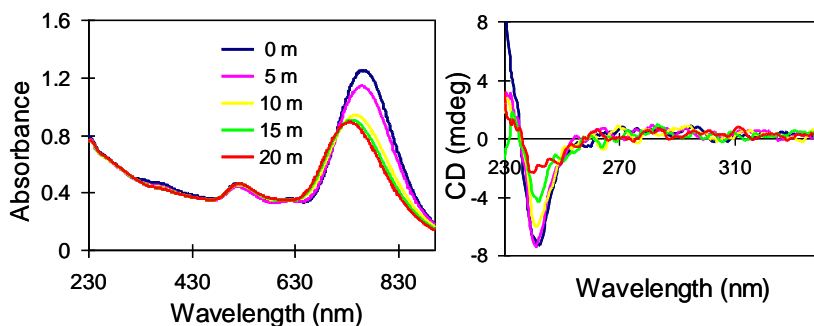


Figure UV-vis (left) and CD (right) spectra of (*R*)-**1** monolayer-protected gold nanorods under UV irradiation at 254 nm for 0 (blue), 5 min (pink), 10 min (yellow), 15 min (green), and 20 min (red).

- **Organo-soluble porphyrin mixed monolayer-protected gold nanorods** were, for the first time, synthesized and characterized. The resulting gold nanorods (GNRs) encapsulated by both porphyrin thiol and alkyl thiol on their entire surface with strong covalent Au-S linkages (Fig. 1) exhibited unique optical properties in sharp contrast to their corresponding spherical gold nanoparticles (e.g. Fig. 2). With the short alkyl thiol molecules, porphyrin mixed monolayer-protected gold nanorods enabled the insertion of C₆₀, creating the electron donor-acceptor alternative structure on the gold nanorod surface. Through this hybrid nanomaterial, it opens a new avenue for the research in investigating the effects of functional organic molecule on the plasmon property of anisotropic gold nanoparticles. This hybrid structure would hold a promise for energy conversion in hybrid photovoltaic devices because it provides the increasing donor-acceptor interface for the porphyrin-C₆₀ with the huge contact area on nanoparticles. In addition, the nanorod structure forms a direct path for charge transport, a desirable condition for efficient photovoltaic devices. This combination of organic electron donor-acceptor system and inorganic nanorods could be used to enhance the capability of photovoltaic devices and improve their performances.

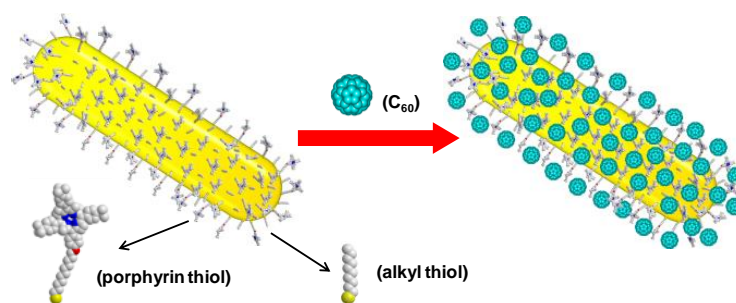


Figure 1. Schematic representation of porphyrin mixed thiol monolayer-protected GNRs (P-C₁₀-GNR) intercalated with C₆₀ and chemical structure of our synthesized porphyrin thiol surfactant and commercially available 1-decanethiol.

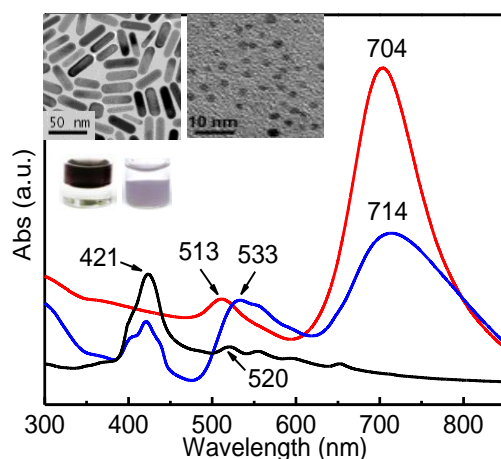


Figure 2. UV-Vis spectra of CTAB-coated GNRs (CTAB-GNR) in H₂O (red), and porphyrin mixed thiol monolayer-protected GNRs (P-C₁₀-GNR) (blue) and porphyrin thiol monolayer-protected spherical gold nanoparticles (P-GNP) (black) in CHCl₃. The insets show photographs of the solutions of corresponding CTAB-GNR (left) and P-C₁₀-GNR (right) in the two phases (top layer: water; bottom layer: CHCl₃), and TEM images of P-C₁₀-GNR (left) and spherical P-GNP (right).

- Porphyrin Zn, Cu and Mg complex monolayer-protected gold nanorods (GNRs)** were, for the first time, synthesized. Their synthesis was easy to access just by mixing porphyrin encapsulated GNRs (POR-GNRs) with corresponding excess soluble metal salts in solution, followed by the facile purification through centrifugation and sonication due to the gravity of the GNRs and their solubility in organic solvents. This synthetic method demonstrated here is generally widely effective to construct many other metal complex protected metal nanoparticles, which enables the rapid synthesis of a wide number of metal complex protected metal nanoparticles in parallel. The resulting three GNRs respectively encapsulated with Zn, Cu and Mg porphyrin complexes via strong covalent Au-S linkages (MP-GNRs) exhibited distinct spectroscopic properties. Furthermore, these MP-GNRs were found to be able to self-assemble into side-by-side arrays driven by π - π intermolecular interactions of the surface porphyrin chromophores. Complementary to the widely used ionic interactions in aqueous medium, the π - π interactions provide an efficient way for processing self-assemblies of GNRs in various organic

media. The new family of GNRs functionalized with metal porphyrin complexes would not only open the avenue for creating and studying the special metal atoms-GNR structure, but also provide an exciting impetus for developing self-assembled GNRs and utilizing their properties for practical applications such as SERS and LSPR sensing.

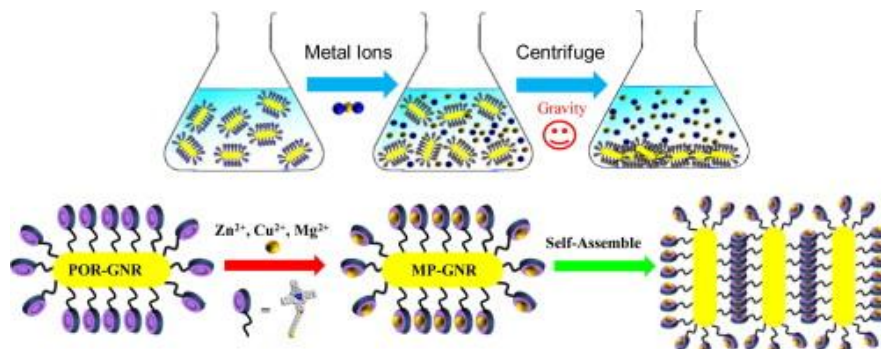


Figure Schematic illustration of preparation of MP-GNRs starting from POR-GNRs with metal salts in a facile synthesis.

- **Organo-soluble perylene thiol monolayer-protected gold nanorods (PDI-GNRs)** were, the first time, synthesized and characterized. The resulting PDI-GNRs showed unique optical and electronic properties compared with the initial free perylene molecules and CTAB coated GNRs. From FT-IR and DSC experiments, intermolecular interdigitation of perylene thiols on GNR surface was confirmed, which exhibited crystalline packing of PDI molecules on surface owing to π - π interactions. As the result, with the assistance of the non-covalent strong π - π intermolecular interactions of perylene molecules, the hybrid PDI-GNRs were able to self-assemble. Well-organized side-by-side assembly arrays could form from the diluted solution. Unlike the widely used ionic interactions in aqueous medium, the π - π interactions provide an easy efficient way for processing self-assemblies of GNRs in versatile organic media. This method can be expanded for other nanostructures to build various assembly structures with new properties for diverse applications.

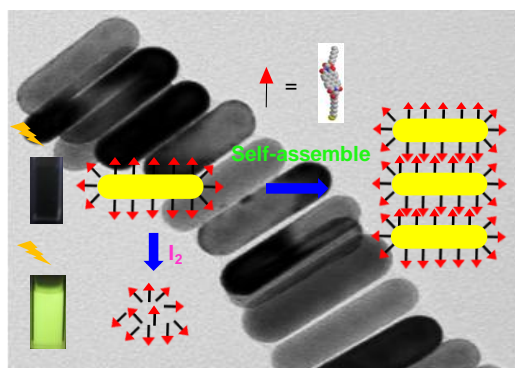


Figure TEM image of a self-assembled PDI-GNR array. Inset: PDI-GNR CH_2Cl_2 solution shows no fluorescence under UV light while its CH_2Cl_2 solution after adding I_2 shows strong yellow-green fluorescence, and schematic presentation of self-assembled PDI-GNRs.

- **Organo-soluble thiol monolayer-protected gold nanoparticles of different shape and size** were homogenously mixed with strong fluorescent perylene diimide (PDI) dye molecules in both solution and solid state. The effect of the doped gold nanoparticles on PDI was investigated by UV-vis, fluorescence, transmission electron microscopy, scanning electron microscopy, and Raman experiments. The gold nanoparticles were found to modify the strong fluorescence properties of PDI depending on the particle size and shape. The smallest spherical gold nanoparticles (2.6 nm) exhibited the strongest quenching effect. When the smallest spherical gold nanoparticles were cast on the PDI soaked paper followed by drying and/or sealing in a polydimethylsiloxane film, the area with gold nanoparticles showed significant quenching effect under a UV light but appeared visually identical to the surrounding area under daylight. The combination of fluorescent dyes and GNPs could be used in macroscopic applications such as antifraud technology by inkjet printing. This research would open up a new avenue introducing nanomaterials into practical applications.

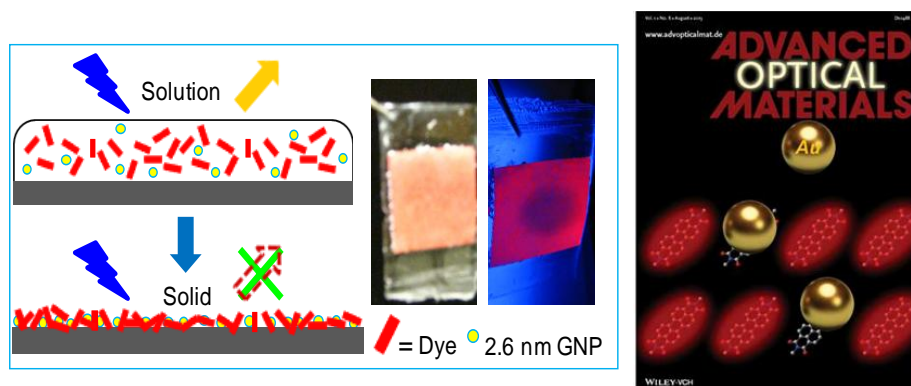


Figure Left: Schematic depiction of the molecular state of PDI molecules mixing with GNP_1 in the solution and solid states. Middle: Picture of a PDMS film containing a square piece of filter paper covered by PDI molecules and treated with one drop of low concentration GNP_1 (left: under a daylight lamp and right: under a UV lamp). Left: highlight in the cover.

- **Photo-modulated self-assembly of hydrophobic thiol monolayer-protected gold nanorods and their alignment in liquid crystal.** Three new terminal thiols possessing azobenzene and perylene diimide (PDI) segments covalently linked by alkylene spacers of different length (P_nSH) were synthesized to stabilize and functionalize gold nanorods (GNRs) via covalent Au-S bonds onto the gold surface. The resulting hydrophobic thiol monolayer-protected GNRs (P_nGNRs) exhibited fascinating photoresponsive self-assembly behavior. Interestingly, when P_nGNRs were mixed with a structurally similar room-temperature thermotropic liquid crystal perylene diimide (LCP), the UV-irradiated P_nGNRs showed more compatibility with the LCP host than their corresponding un-irradiated ones. Furthermore, the P_nGNRs with varied alkylene chain lengths showed different dispersion abilities in LCP. The UV-irradiated P_4GNRs did not disperse well in LCP whereas the UV-irradiated P_6GNRs and P_8GNRs dispersed well in LCP and were further aligned upon mechanical shearing. This work provides a method to tune GNR self-assemblies and further offers a way to disperse and align GNRs in a LC film. These studies not only give insight into controlling the self-assembly of anisotropic nanoparticles which have altered SPR properties arising from the switchable assembled structures but also suggest a

method to align the anisotropic nanoparticles which could further guide to fabricate novel nanophotonic and optical metamaterials.

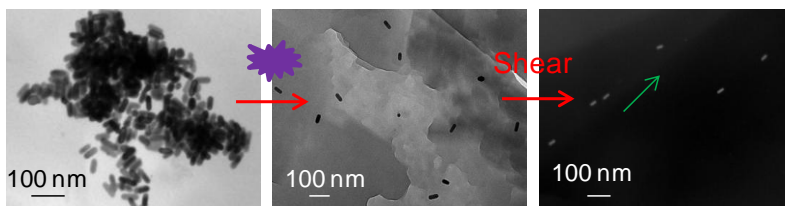


Figure TEM images of P₈GNR in LCP. (A) Before UV irradiation. (B) After UV irradiation. (C) After shearing. C is from scanning TEM.

- **Controllable self-assembling of gold nanorods via on and off supramolecular noncovalent interactions.**

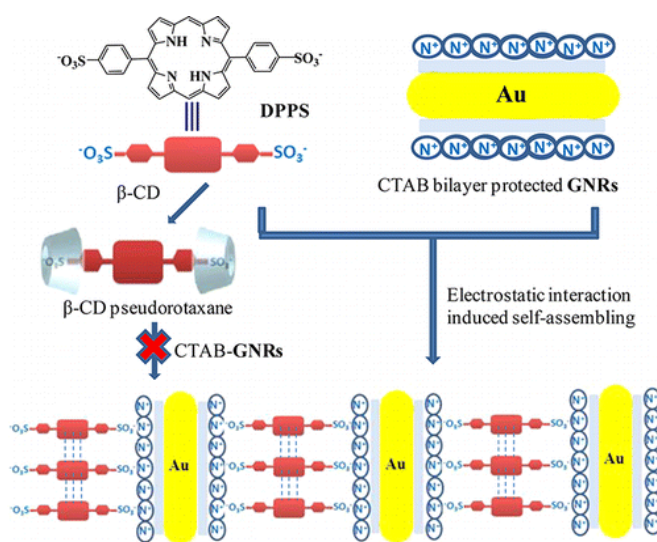


Figure. Schematic illustration of the controllable self-assembling of GNRs via on and off supramolecular noncovalent interactions.

5,15-Bis(4-sulfonatophenyl)porphyrin (DPPS) with a planar conjugated system and two negative charges was found to be able to engender the self-assembling of CTAB-GNRs due to the electrostatic interaction between DPPS and CTAB together with the π - π intermolecular interaction of DPPS, while its bulky supramolecular pseudo[3]rotaxane included by β -cyclodextrin prevented such self-assembling due to the interruption of the above noncovalent interactions. CTAB-GNRs aqueous solution was of well-dispersed morphology. Increasing the amount of DPPS with negative charges was able to induce the self-assembling of CTAB-GNRs, and exhibited totally different fluorescent emission peaks in both the position and the shape. This aqueous system was able to be excited to engender adjustable fluorescence emission in the near-infrared region. While the addition of DPPS pseudo[3]rotaxane using β -CD host was not able to induce the self-assembling of CTAB-GNRs since the supramolecular inclusion interaction between β -CD and DPPS interrupts the π - π intermolecular interaction of DPPS molecules as

well as the electrostatic interaction between CTAB-GNRs and DPPS. This concept demonstrated here, i.e., controllable self-assembling via on or off supramolecular noncovalent interactions would open a convenient way to control GNR self-assembling and achieve some specific morphology-dependable function.

- pH and temperature modulated aggregation of hydrophilic gold nanorods with perylene dyes and carbon nanotubes.** Hydrophilic mercaptosuccinic acid (MSA) monolayer-protected gold nanorods (GNRs) were synthesized. The resulting GNRs encapsulated with biocompatible MSA molecules via covalent Au–S linkages were found to be able to self-aggregate through intermolecular hydrogen bonding. Interestingly, when the hybrid GNRs (MSA-GNR) were mixed with the hydrophilic fluorescent perylene diimide (PDI) molecules and carboxylic acid modified single-wall carbon nanotubes (CNT-COOH), respectively, their aggregation behaviors were pH- and temperature-dependent, which were investigated by UV–vis, fluorescence spectra, and TEM images. The aggregates of MSA-GNR with functional PDI and CNT-COOH were able to combine the properties of each component through noncovalent interactions, providing insight into developing new multifunctional metal nanocomposites with properties tailored for their practical application. This research on aggregation behavior of multifunctional nanostructures containing multiple components through intermolecular noncovalent interactions provides new insight into the development of novel multifunctional metal nanocomposites.

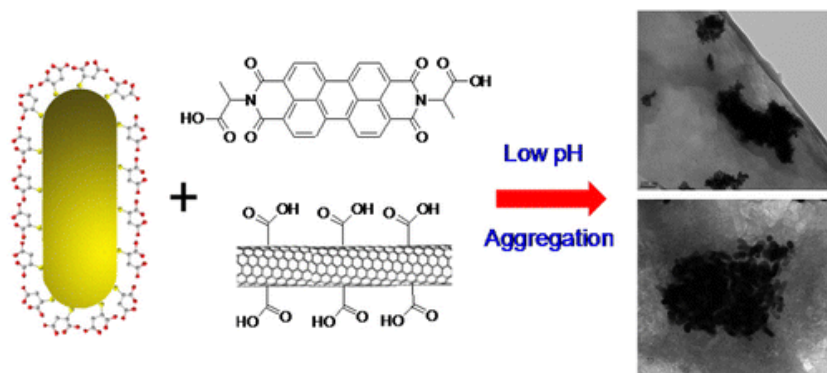
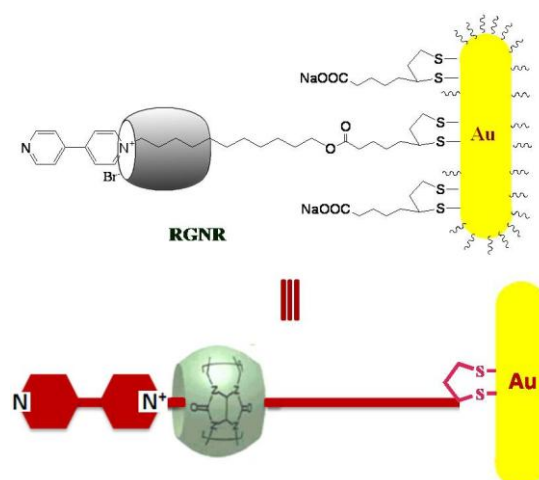


Figure. Schematic presentation of modulated aggregation of hydrophilic gold nanorods with perylene dyes and carbon nanotubes

- Cucurbit[7]uril-pseudorotaxane anchored monolayer-protected gold nanorods** was for the first time prepared and characterized. The resulting GNRs decorated with both cucurbit[7]uril-based pseudorotaxane disulfide and sodium thiocyanate on their entire surface through covalent S–Au linkages are water-soluble as well as stable in both solution and the solid state. The shorter sodium thiocyanate, which fills up the potential space on the GNR surface between the pseudorotaxane molecules, not only acts as a stabilizer but also provides better water solubility. The hybrid system demonstrated here, which combines a supramolecular machine and GNR together, should open new and interesting research avenues for the construction of multifunctional organic–inorganic hybrid materials.



Scheme. Schematic illustration of the CB[7] pseudo[2]rotaxane mixed monolayer-protected RGNRs.

- Building 3D layer-by-layer gold-graphene nanoparticle hybrid architecture with tunable interlayer distance.** The ability to construct self-assembled three-dimensional (3D) superstructures with desired functionality is not only of scientific curiosity but also crucial in the bottom-up nanofabrication of smart materials and devices. Here a facile solution-processable strategy for creating 3D layer-by-layer graphene–gold nanoparticle architectures was developed in which cysteine molecules with amino groups were chemically grafted onto the surface of graphene oxide and then the cysteine thiol groups were attached to the surface of gold nanorods (GNRs) through strong covalent Au–S linkages. In this self-assembled structure, as revealed by transmission electron microscopy (TEM) and scanning electron microscope (SEM), it was confirmed that the graphene layers aligned in parallel fashion rather than randomly to each other by the lying down patterns of the GNRs, which also formed layers in parallel. Furthermore, when GNPs with different sizes were introduced, the distance between graphene layers could be controlled, offering an opportunity to investigate the effect of the interlayer distance on properties of the 3D graphene materials. Oxidation reduction reaction (ORR) and cyclic voltammetry (CV) measurements indicated that these 3D hybrid nanomaterials possess good electrochemical activities, which have potential in applications such as fuel cells and supercapacitors. This work provides an exciting impetus for building a tunable 3D carbon nanostructure with tailored functionality.

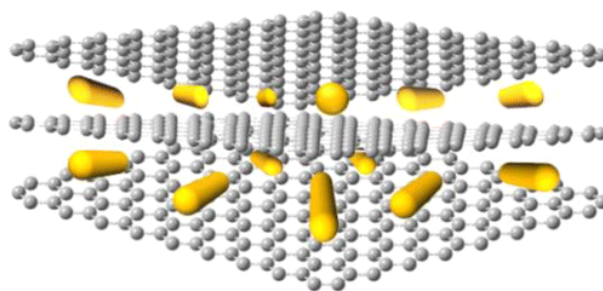


Figure Schematic the representative of layer-by-layer graphene–GNR hybrid architecture.

- **Near-infrared light induced transformation between liquid crystal and isotropic phase enabled by mesogenic functionalized hybrid gold nanorods.** Light, used as a driving force to control liquid crystal phase transformation has been a burgeoning area of research to develop new molecular switches. Here we have synthesized organo-soluble mesogenic hybrid gold nanorod (M6-GNR), which were found to be able to nicely mix with liquid crystal host. The resulting nanocomposite was able to increase the stability of the liquid crystal phase. More interestingly, the irradiation of near-infrared light resulted in a photothermal effect, resulting from gold nanorods having a longitudinal absorption peak around near-infrared region, which promoted the phase transition

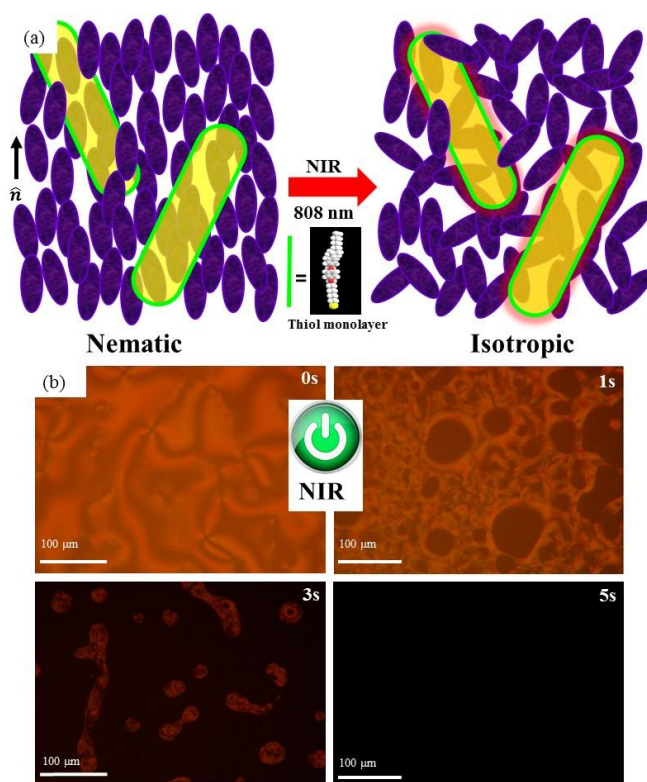


Figure (a) Schematic representation of nematic-isotropic transition under NIR irradiation; (b) Textures observed under cross polarized microscope at different exposure times of 808 nm NIR laser (2W) of M6-GNR in liquid crystal host.

- **Near-infrared light-directing transformation of three-dimensional self-organized cubic nanostructures enabled by mesogen-functionalized gold nanorods.** Stimuli-directing three dimensional (3D) photonic supramolecular architectures with tailored functionalities are a driving force in the bottom-up nanofabrication of intelligent molecular materials and devices. Liquid crystalline blue phases (BPs) that can self-organize into the 3D periodic cubic nanostructures undoubtedly represent such an elegant functional system due to their unique properties of photonic band gap selective reflection of incident light and the consequent application potentials. Herein, novel mesogen-functionalized gold nanorods (GNRs), doped in a commercially available BP media, were able to stabilize the 3D cubic nanostructure over a much

wider temperature range by enhancing the intermolecular forces of liquid crystals and reducing the free energy around the disclination. More interestingly, the resulting GNR-impregnated cubic superstructure underwent unprecedented reversible structural transformation upon the irradiation of the continuous-wave NIR laser because of the photothermal effect from surface plasmon resonance of GNRs. Upon NIR laser irradiation at 808 nm, its 3D nanostructure changes from body-centered-cubic to simple cubic before isotropic phase is achieved, whereas its reverse process occurs soon after removing the NIR laser irradiation. The unique, reversible, and dynamic control of NIR light-directing structural transformation of such soft self-organized 3D photonic crystals bestows fascinating applications toward the realization of truly integrated photonic circuits, etc.

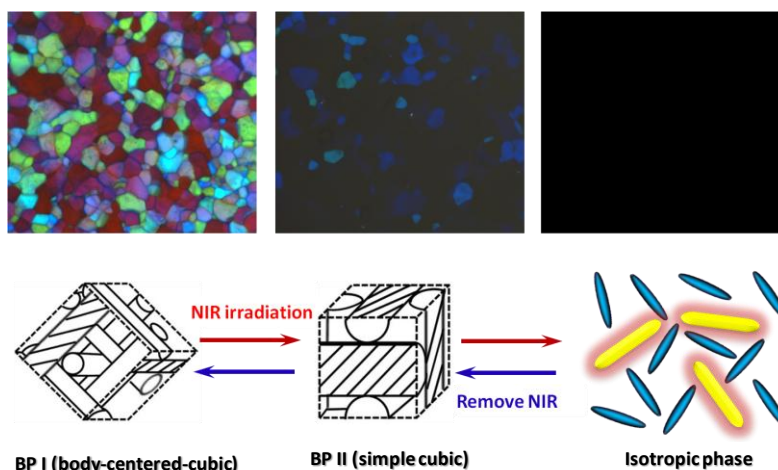


Figure NIR-directing structural transformation of gold nanorod doped blue phase. Top: Phase change up NIR irradiation. Bottom: Schematic illustration of the structural transformation upon NIR irradiation.

Publications during Reporting Period with Acknowledgements to the AFOSR Grant

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Synergistic Activities and Honors Which greatly benefited from the Project

- 2014 Kent State University Outstanding Research and Scholarship Award
- The editor of the Springer book entitled *Anisotropic Nanomaterials: Preparation, Properties, and Applications*, Springer, **2015**
- The editor of the Springer book entitled *Nanoscience with Liquid Crystals: From Self-organized Nanostructures to Applications*, Springer, **2014**.
- The editor of the book entitled *Intelligent Stimuli-Responsive Materials: From Well-defined Nanostructures to Applications*, John Wiley & Sons, **2013**.
- The editor of the book *Liquid Crystals Beyond Displays: Chemistry, Physics, and Applications*, John Wiley & Sons, **2012**.
- The editor of the book entitled *Self-Organized Organic Semiconductors: From Materials to Device Applications*, John Wiley & Sons, **2011**.
- The invited author of the entry entitled "Gold Nanorods" in *Encyclopedia of Surface and Colloid Science*, second edition, Taylor & Francis, **2014**.
- The invited author of the entry entitled "Liquid Crystals" for the prestigious *Kirk-Othmer Encyclopedia*, John Wiley & Sons (which had online published in this encyclopedia on Sept. 15, 2014).
- International Advisory Committee Member and Plenary Speaker at 2014 International Conference on New Energy and Sustainable Development.
- Chair the session "Material, Devices and Switches" at 2014 ACS National Fall Meeting at San Francisco.
- Invited Speaker at 2014 International Liquid Crystal Conference, Dublin.
- Chair the session "Physical Organic Chemistry" at 2013 ACS National Fall Meeting at Indianapolis.
- 2013 Invited Speaker at 2013 Gordon Research Conference on Liquid Crystals.
- Chair two sessions "Materials, Device, and Switches" and "Gold Nanoparticles: Stabilization, Assembly, and Application" at 2012 ACS National Fall Meeting at Philadelphia.
- Advisory Committee Member and Plenary Speaker at Liquid Crystal Photonics 2012, Guilin.
- International Scientific Committee Member and Invited Speaker at 2011 International Conference on Smart Materials and Nanotechnology in Engineering, Shenzhen.
- International Advisory Committee Member and Plenary Speaker at 2011 International

Symposium on Liquid Crystals: Science and Technology, Changzhou.

- Invited Speaker at Pacificchem 2010 Congress, Hawaii.
- International Scientific Advisory Committee Member and Plenary Speaker at 2010 International Conference on Optical, Electronic and Electrical Materials, Kuming.
- Interviewed by *Materials Views* on October 18, 2011 at <http://www.materialsviews.com/materialsviews-interviews-quan-li/>
- Served as an active panelist/reviewer for funding agencies such as DOE, DoD, NSF, ACS PRF, Swiss NSF, and Chile National Fund, and many publishing houses.